

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Application of Jian Qin, et al. Art Unit 3761
Serial No. 10/631,916
Filed July 31, 2003
Confirmation No. 9626
For ABSORBENT MATERIALS AND ABSORBENT ARTICLES INCORPORATING
SUCH ABSORBENT MATERIALS
Examiner Ginger T. Chapman

August 29, 2006

DECLARATION UNDER 37 C.F.R. §1.131

We, Jian Qin, Xiaomin Zhang, and Debra Ann Miller declare
as follows:

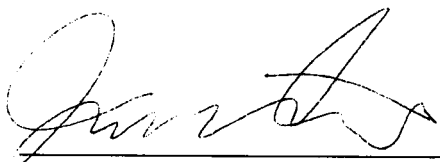
1. We are the joint inventors of the subject matter
claimed in the above-entitled United States patent application,
Serial Number 10/631,916.
2. At the time of filing application Serial Number
10/631,916, we were employed by Kimberly-Clark Worldwide, Inc.
and have assigned all rights to the application to Kimberly-
Clark Worldwide, Inc.
3. We are submitting this Declaration to establish
conception of the invention of the subject matter of claim 13 in
the United States prior to November 21, 2001, coupled with
diligence from prior to such date to the filing date of the '916
application.
4. Exhibit A, attached hereto, provides facts and evidence
in support of this Declaration. Exhibit A is an invention
disclosure form disclosing the subject matter of the present

application. Invention disclosures are prepared by inventor/employees of Kimberly-Clark Worldwide, Inc. in the regular course of business. While all dates identified in the disclosure of Exhibit A have been blocked out, the date of conception, set forth in item 3 on page 2 of Exhibit A, is prior to November 21, 2001.

5. We worked with outside counsel in the preparation of the '916 application and received a draft of the application on or about April 2003. We continued to work with outside counsel to finalize the application for filing on July 31, 2003.

6. We were not aware of published PCT application No. WO 03/043670 prior to the filing of the '916 application.

7. We further declare that all statements made herein are of our own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under 18 U.S.C. § 1001, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.



Jian Qin

Sept. 20, 2006
Date

Zhang, Ximin

Xiaomin Zhang

9/30/2006

Date

KCC 4963
K-C 19,109

Debra Ann Miller
Debra Ann Miller

September 20, 2006
Date

Invention Disclosure

Instructions to Submitter:

Send the signed original and one copy of this form to Kimberly-Clark Corporation, Patent Department, Neenah, WI. Answer all parts of this form. Two corroborators must understand the invention. The submitter(s) and both corroborators must sign and date this form immediately following item 15 in blue ink, as well as every additional sheet submitted with it. The last part of this form is recommended when additional sheets are required. If your group has a patent facilitator, preview the original with him or her.

Disclosure No.

19189

Department

Recommended Attorney

For Legal Department use only

PAR Number

Name of Affiliate/Subsidiary/Licensee, if applicable:

Key Words

Superabsorbent Polymer (SAP), Absorbency Under Load (AUL), Centrifugal Retention Capacity (CRC), Gel Bed Permeability (GBP), GBP Under Swell Pressure, Gel Stiffness Index, Surface Treatment, Cationic Polymer

1. Title

Superabsorbents Having Improved Permeability Under High Swell Pressure

2. Description (Sign and date each page. Attach pertinent drawings, photographs, block diagrams, flow charts, etc.)

a. Summary (Should disclose invention in general, nontechnical terms)

This invention discloses superabsorbent polymers having improved liquid permeability under a high swell pressure compared to that of current commercial available superabsorbents. The improved superabsorbents exhibit a centrifugal retention capacity (CRC) of at least 20 g/g and a gel bed permeability under a 0.3 psi swell pressure (GBP @ 0.3 psi) of at least 200 ($\times 10^{-9}$ cm²). The invention also discloses a method to achieve the above combination of the disclosed properties. The method involves (1) selecting a superabsorbent having a CRC greater than 20 g/g and a gel stiffness index greater than 0.8 and (2) surface treating the selected superabsorbent with a cationic polymer solution.

b. Detailed description, including specific embodiments and applicable alternatives, ranges and products, and process/apparatus variations.

As current personal care absorbent products, such as infant diaper, training pant, adult incontinence product, etc., are becoming thinner, denser and with narrower crotch width, permeability of the absorbent products is becoming more and more important and closely correlates to product performance. In order to quickly allow insulting liquid get into an absorbent core, superabsorbent polymer used in the absorbent core has to be properly crosslinked so that it does not deform too much and stick together to cause so-called "gel blocking" when the core is wet. This gel blocking phenomena inhibit liquid transmission into insulting region or to other regions of an absorbent core. Once the gel blocking occurs, the liquid can only penetrate into the core via a very slow diffusion process.

(Continued on page 4)

c. How does the invention distinguish from what has been done in the past and what advantages are obtained? Identify related work done by others (patents, journal articles, etc.). Identify other related disclosures of which you may have knowledge, or other work within Kimberly-Clark Corporation within the same area.

All commercial and experiment superabsorbents ACD has investigated so far do not have a combination of a CRC greater than 20 g/g and a GBP @ 0.3 psi greater than 200 ($\times 10^{-9}$ cm²). Prior art (EP 0 744 954 B1) disclosed use of polyallylamine to surface treat superabsorbents but did not teach selection of gel stiffness index of a superabsorbent. The superabsorbent used in examples of the prior art has a capacity of greater than 35 g/g. Its gel stiffness index must be below 0.8.

Invention Disclosure

Title: Superabsorbents Having Improved Permeability Under High Swell Pressure

3. I (We) first conceived the above idea on _____
4. I (We) first disclosed the above idea to others on _____
5. The persons to whom the above idea was first disclosed are: **Jerry Zabronsky**.
6. The first written description of the above idea is in the form of **Lab Notebook P-7396, page 79** dated _____ and is now located in **ACD**.
7. The first sketch or drawing of the above idea was made on _____ and is now located in **Lab Notebook P-7396, pages 174 to 175**. Its number is **NA**.
8. The first sample/embodiment illustrating the above idea was made on _____ and is now located in **ACD**. Its identification number is **Sample 10 & 11 in Lab Notebook P-7396, page 175**.
9. The above idea was first actually tried on _____. Describe how and when it was tried, including a complete description and date of the first time the idea was tried and, if the first attempt was unsuccessful, the first time it was successfully tried.
- Commercial superabsorbents, Favor 880 and SXM 9543 from Stockhausen Inc., were surface treated with a polyvinyl amine solution available from BASF designated under trade name of CAT10FAST*PR8106 (25 wt% solids). The solution was pre-dissolved into distilled water and dry superabsorbent was added and stirred. The treated and swollen superabsorbent was dried at 60°C for overnight. The dried superabsorbent was screened through an 850 microns sieve and any particles larger than 850 microns were pressed by hand to separate agglomerated particles.
10. Has consumer or public use testing of this idea been carried out? **No** If "Yes," when? **NA** Describe testing: **NA**
11. Is consumer or public use testing planned for the future? **No** If "Yes," when? **NA** Describe testing: **NA**
12. Has the idea been used in, or to produce, a product or a service that was sold or offered for sale? **No** If "Yes," when? **NA** How used: **NA**
13. Has the idea been disclosed outside Kimberly-Clark Corporation? **Yes** If "Yes," when? _____ To whom: **Stockhausen Inc.**

Describe details surrounding all disclosures. Presented importance of superabsorbent having a GBP at a higher swell pressure and requested Stockhausen Inc. to develop pressure resistant superabsorbents, such as GBP @ 0.3 psi greater than 200.

Was the idea disclosed under Confidential Disclosure Agreement? **Yes** If "Yes," attach a copy of the agreement.

14. Is public or commercial use imminent? **No**. If "Yes," indicate the anticipated earliest date of commercial use. **NA**
15. List the names of everyone who has contributed to this idea. (Those listed cannot be corroborators. The listed people should receive a copy of this form.)

Jian Qin, Xiaomin Zhang, and Debbie Graverson of ACD,

Submitter


Signature

Jian Qin

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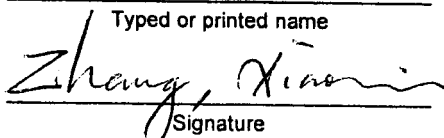
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Title: Superabsorbents Having Improved Permeability Under High Swell Pressure

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Invention Disclosure

Title: Superabsorbents Having Improved Permeability Under High Swell Pressure

2b) Detailed Description (continued from page 1):

In practical terms, this means intake of liquid by the absorbent core is much slower than the rate at which liquid is discharged. Leakage from the absorbent product will take place well before the superabsorbent polymer in the absorbent core is fully saturated. Gel blocking can be a particularly acute problem when the absorbent core is under a higher pressure or at a higher level of saturation. Therefore, to develop a superabsorbent polymer which has an improved liquid permeability property, especially under a high swell pressure, is so important to both current absorbent article performance and future product development. The purpose of this invention is to develop superabsorbent polymer having a significantly improved GBP @ 0.3 psi over current commercial available superabsorbents. The higher the GBP value of a superabsorbent, the easier a liquid can pass through the layer of the swollen superabsorbent.

Past SAP development showed that increasing gel strength of a superabsorbent polymer can contribute to decreasing gel blocking and thus increasing liquid permeability. Gel strength enhancement is mainly achieved by increasing crosslinking density of a superabsorbent. Though this approach could greatly enhance permeability, the gains are obtained at the cost of significant reduction in absorbency since crosslinking tends to lower overall swellability. This limits the use of this approach. For example, previous commercial superabsorbent Favor 880 has a high capacity but a low gel strength and poor liquid permeability. Stockhausen later developed a new version of superabsorbent SXM 9543 with increased degree of crosslinking which exhibits a reduced capacity but improved gel strength and liquid permeability. SXM 9543 performed better than Favor 880 in product use tests. Therefore, SXM 9543 has replaced Favor 880 since then. However, further increasing crosslinking density over SXM 9543 did not improve product performance due to significant loss in capacity. It was found that enhancing permeability only by crosslinking reached its limitation. Other approaches have to be developed in order to further enhance permeability without sacrificing too much in capacity.

This invention discloses a novel surface treatment on current existed commercial superabsorbents with a cationic linear polymer solution. Such surface treatment does not reduce absorbency of the treated superabsorbent but significantly increase its GBP values with or without swell pressure. Current available commercial superabsorbents are all crosslinked sodium polyacrylate based polymers. They are water-swellable but water-insoluble anionic polymer gels. When a cationic polymer is coated onto the surface of these polymers, surface is mainly covered by the cationic polymer when the superabsorbents are not swelled too much during the modification step which prevents the cationic polymer from penetrating towards inside of the particles. There is no strong ionic attraction between the treated particles when they are dry or at low degree of saturation since all surfaces are covered by cationic polymer. However, when this coated polymer gel is saturated or swelled to a high degree, the anionic polymer inside the superabsorbent particles starts to expose to the surface of particles. Surface of a swollen particle will have both cationic and anionic regions as illustrated in Fig. 1 below. Cations on one swollen particle will attract anions on the other swollen particles, vice versa. This attraction between counter-ions greatly enhances binding power between particles which causes particles tend to "stick" together. Once this occurs, inter-particle movement becomes impossible and further swelling of the stuck particles will either generate a lot of open "air pockets" within gel particle layer or form a dense and tightly packed layer dependent upon gel stiffness of the superabsorbent. High gel stiffness of a superabsorbent can resist deformation of its particle shape and swell against pressure of the restraint to create open voids between particles. Either maintaining or creating open voids will increase liquid permeability. On the other hand, a superabsorbent with low gel stiffness will swell but deform its particle shape greatly to occupy as much internal gaps or voids as possible to achieve swelling. In this case, internal voids are eliminated and liquid permeability is lowered. Such effect of pressure on permeability is amplified when a superabsorbent is subjected to a high swelling pressure (pressure is applied on a dry superabsorbent before saturation). It was discovered that the surface treatment enhance both GBP @ 0 psi and 0.3 psi values of a treated superabsorbent when a superabsorbent has enough gel stiffness. On the contrary, the treatment only increase GBP @ 0 psi

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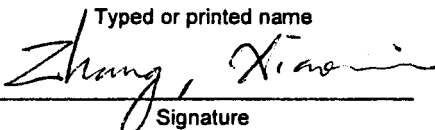
Invention Disclosure

Title: Superabsorbents Having Improved Permeability Under High Swell Pressure

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Xiaomin Zhang

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Debbie Graverson

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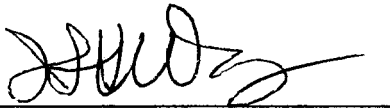
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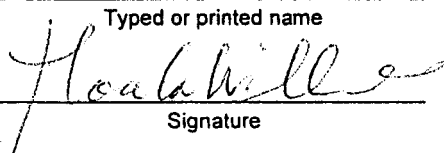
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The foregoing signed disclosure was read and understood by me on the date hereinafter set forth.

Corroborator 
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Hoa La Wilhelm

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Month Day Year

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Invention Disclosure

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value of the treated superabsorbent but lower GBP @ 0.3 psi value due to the above explained reason when a superabsorbent does not have enough gel stiffness. Therefore, it can be concluded that the cationic polymer surface treatment promotes creation of inter-particle voids for a superabsorbent when it is swelled under no load, but only promotes the creation for a superabsorbent having adequate gel stiffness when it is swelled against an external pressure. Gel stiffness index greater than 0.8 can be used as a criterion to select suitable superabsorbents

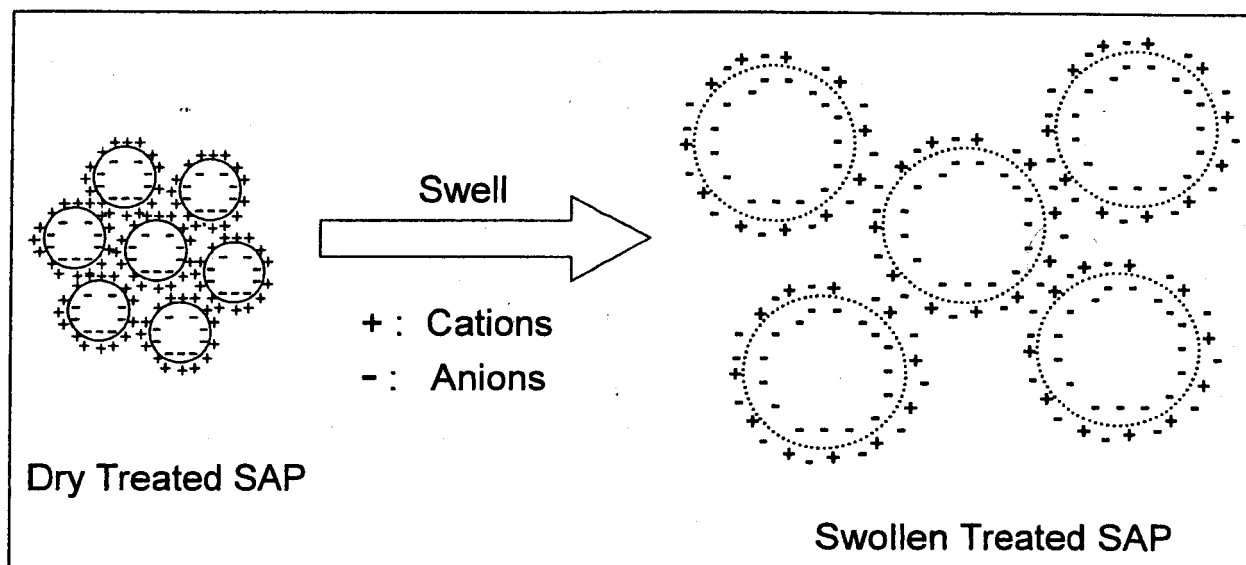


Fig. 1 Distribution of ionic charges on surface of dry and swollen treated SAPs

Tables 1 and 2 summarize absorbency, gel stiffness and permeability data of both commercial and experiment superabsorbents from different vendors. It can be concluded that no superabsorbent exhibits a combination of a CRC greater than 20 g/g and a GBP @ 0.3 psi greater than 200 ($\times 10^{-9} \text{ cm}^2$).

Table 1 Absorbency & Permeability of Commercial SAPs

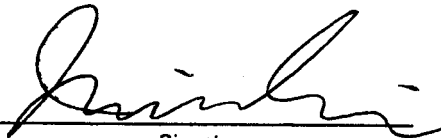
Property \ Superabsorbent	Commercial Superabsorbents			
	Stockhausen Inc.		Dow Chemical	
	SXM 9543	Favor 880	2035	2035HP
CRC (g/g)	22.6	31.9	27.9	26.2
AUL @ 0.9 psi (g/g)	21.6	21.3	17.8	15.8
Gel Stiffness (AUL/CRC)	0.96	0.67	0.64	0.60
GBP @ 0 psi ($\times 10^{-9} \text{ cm}^2$)	316	33.7	27.0	386
GBP @ 0.3 psi ($\times 10^{-9} \text{ cm}^2$)	145	9.4	6.0	35

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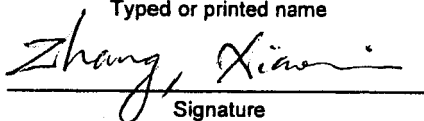
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Corroborator


Signature

James H. Wang

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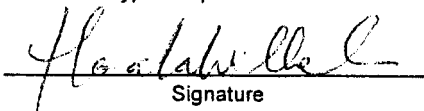
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Table 2 Absorbency & Permeability of Experiment SAPs

Modification		Property	CRC (g/g)	AUL @ 0.9 psi (g/g)	Gel Stiffness Index ¹	GBP @ 0 psi ($\times 10^{-9}$ cm ²)	GBP @ 0.3 psi ($\times 10^{-9}$ cm ²)
Vendor	SAP						
Stockhausen	SP 1283		22.5	19.6	0.87	403	159
	SP 1284		19.1	18.0	0.94	875	253
	SP 1390		28.8	20.7	0.72	846	120
	SP 1392		29.0	19.2	0.66	577	46.6
	SP 1393		30.4	19.0	0.63	716	47.3
	SP 1394		28.6	19.5	0.68	917	67.0
	SP 1396		27.5	19.2	0.70	1140	78.5
	SP 1402		27.3	18.5	0.68	1173	32.5
Dow Chemical	40698.02		21	16.6	0.79	632	116
	AFA227-116A		27	17.4	0.65	545	39.7
	AFA227-116B		28	16.7	0.59	348	21.3
	Kangaroo		28	10.9	0.38	423	28.7

Note: Gel Stiffness Index = AUL @ 0.9 psi/CRC

An aqueous polyvinyl amine solution, available from BASF designated as CAT10FAST*PR8106®, was used to treat commercial superabsorbents. Both high gel stiffness superabsorbent, such as SXM 9543 having a gel stiffness index of greater than 0.8, and low gel stiffness superabsorbents, such as Favor 880 and Dow 2035 having a gel stiffness index of less than 0.7, were selected for the treatment. The polyvinyl amine solution was pre-dissolved in distilled water. Dry superabsorbent particles were added into the solution and stirred vigorously. Weights of superabsorbent, polyvinyl amine solution and distilled water were accurately measured for calculation of CAT10FAST add-on level and superabsorbent-water swell ratio. Results from evaluating the treated superabsorbents show that only SXM 9543 can achieve a combination of a CRC greater than 20 g/g and a GBP @ 0.3 psi greater than 200 ($\times 10^{-9}$ cm²) due to its gel stiffness index greater than 0.8. Low gel stiffness superabsorbents (Favor 880 and Dow 2035) demonstrated an improvement in GBP @ 0 psi but not GBP @ 0.3 psi to the desired level. Also amount of polyvinyl amine has to be adequate, not too little or too much. Swell ratio has to be as low as possible since high swell means penetration of polyvinyl amine into the inside of superabsorbent particles. AUL @ 0.9 psi value is measured for 1 hour. The treated superabsorbents tend to reduce AUL values compared to their controls. This reduction is mainly due to reduction in absorption rate under pressure. When these treated superabsorbents were measured for more than five hours, their reduction in 1 hour AUL values was disappeared. However, a superabsorbent having a gel stiffness index greater than 0.8 exhibits an ability to maintain its 1 hour AUL value after a proper surface treatment. That is why such superabsorbent can achieve improved GBP @ 0.3 psi, while a superabsorbent having a gel stiffness index less than 0.7 cannot. Also it is noted that GBP @ 0 psi values of the treated superabsorbents having a high gel stiffness index are significantly increased to a level current conventional superabsorbents never have, such as greater than 2000 or even 3000.

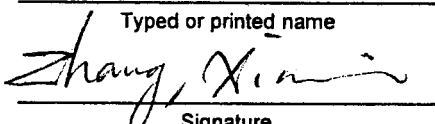
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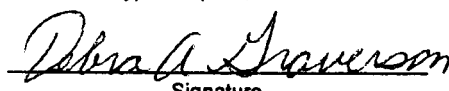
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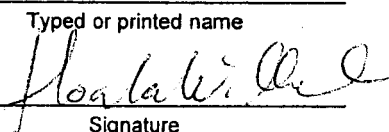
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Corroborator 
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Invention Disclosure

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Table 3 Properties of Commercial SAPs Modified by CAT10FAST®

Modification		Property	CRC (g/g)	AUL @ 0.9 psi (g/g)	Gel Stiffness	GBP @ 0 psi ($\times 10^{-9}$ cm ²)	GBP @ 0.3 psi ($\times 10^{-9}$ cm ²)
SAP	CAT10FAST% ¹	Swell Ratio ²					
SXM 9543	0%	0	23.2	21.6	0.96	316	145
	10%	5	19.8	10.7	0.54	1512	42
Favor 880	0%	0	31.9	21.3	0.67	33.7	9.4
	1.2%	5	30.7	9.2	0.30	31.7	2.1
	2.5%	10	30.4	11.8	0.39	96.9	6.2
	2.5%	5	30.6	12.0	0.39	193.1	7.1
	5%	5	29.8	10.0	0.34	248.3	3.1
	5%	2.5	30.1	9.0	0.30	445.5	1.9
	10%	2.5	30.5	6.7	0.22	286.1	0.2
2035	0%	0	27.9	17.8	0.64	27.0	6.0
	5%	2.5	25.4	14.8	0.58	1045	109

Note: ¹: CAT10FAST*PR8106® from BASF is an aqueous solution containing 25% polyvinyl amine.

²: Swell Ratio = Water : SAP (weight ratio).



An example of this invention.

A Summary of Invention:

Surface treated commercial superabsorbent, SXM 9543, by a polyvinyl amine solution exhibits a significant increase in both GBP @ 0 psi and GBP @ 0.3 psi. A combination of CRC greater than 20 g/g and a GBP @ 0.3 psi greater than 200 ($\times 10^{-9}$ cm²) is a novel set of properties which no prior commercial superabsorbents have been demonstrated. Furthermore, a combination of a CRC greater than 20 g/g and a GBP @ 0.3 psi greater than 250 ($\times 10^{-9}$ cm²), a CRC greater than 20 g/g and a GBP @ 0.3 psi greater than 300 ($\times 10^{-9}$ cm²), or a CRC greater than 20 g/g and a GBP @ 0.3 psi greater than 500 ($\times 10^{-9}$ cm²); or a combination of a CRC greater than 25 g/g and a GBP @ 0.3 psi greater than 200 ($\times 10^{-9}$ cm²), a CRC greater than 30 g/g and a GBP @ 0.3 psi greater than 200 ($\times 10^{-9}$ cm²), or a CRC greater than 35 g/g and a GBP greater than 200 ($\times 10^{-9}$ cm²); or a combination of any CRC and GBP @ 0.3 psi values stated above is an element of this invention.

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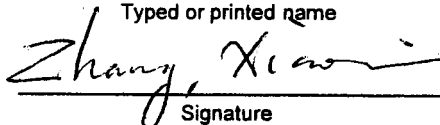
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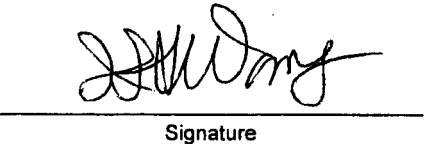
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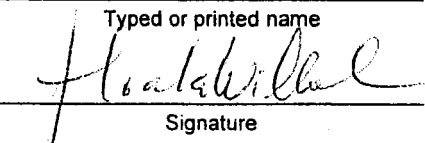
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